

**Studies on Goran Liquors  
Extracted from Commercial Bark**

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Roux<sup>7</sup> by paper chromatography and direct analysis showed that differential leaching of commercial wattle bark produced extract which differ in tan/nontan ratio, as well as in the composition of nontannins. The cold extract contains abnormally high proportion of fermentable sugar (sucrose) and a low admixture of gums, while in the subsequent hot extraction these properties are reversed. No marked differentiation was obtained in the main polyphenolic fraction.

The present work is designed to show the difference between cold and hot extractions (separate and consecutive) and counter-current leaching (cold and hot) of commercial goran bark in their tan and nontan (gums, sugars etc.) contents and the tanning potency of these tan extracts.

## Experimental

### A. PREPARATION OF LIQUOR

#### (i) *Extraction of commercial chopped bark*

In one set of experiments 500 g. lots of goran bark were soaked separately with one litre of distilled water and were extracted for 24 hours at 8°C, 30°C and 80°C respectively. The extract obtained after filtration were analysed for their tans, nontans, total salts, gum content and gelatine numbers. The yield was also determined. In another set of experiments, the bark (500 g) was extracted at 8°C in the same way as before. After the filtration of infusion the bark residue was treated with the same volume of water which was collected after filtering the cold extract (8°C) and kept at room temperature

(30°C) for 24 hours. The volume and strength of the filtered extracts were noted as before. The bark residue was treated again with the same quantity of water as before and kept at 80°C for the same period. All the extracts obtained from this set of experiment were also analysed as before. For comparison, 60 g. of bark was extracted by Procters extraction apparatus and liquor obtained (0.4% tannin solution) was analysed for tannin, nontannin, total salt and gum. The yield of the extract was also determined.

#### (ii) *Counter-current extraction*

A counter-current leaching of the bark was made by using 100 g. of the bark per beaker and starting with 250 ml. water at room temperature followed by a succession of 150 ml. quantities. The liquors were transferred to the next beakers after every four hours during the day time and left to stand overnight. Similarly a counter-current hot leaching of the bark was made separately at 70°C (higher temperature was used only during the day). No. 6 beakers in both the cases were extracted 6 times and the rest of the beakers were extracted 5, 4, 3, 2 and 1 times respectively. Counter-current leaching at room temperature (30°C) in a six flask system yielded liquor of 50°Bk and at higher temperature (70°C) liquor of 65°Bk was obtained. Leaching efficiency (number of g. of tannins leached per 100 g. of tannins) of the barks, after 6th extraction (both cold and hot) and drying, were then determined.

The following were the concentration gradients in a six container counter-current system.

Room temperature (30°C) }	Flask No.	1	2	3	4	5	6
Counter-current extraction }	°Bk	1	3	10	25	42	50
Hot (70°C) }	Flask No.	1	2	3	4	5	6
Counter-current extraction }	°Bk	0	5	18	40	50	65

#### B. CHROMATOGRAPHIC AND CHEMICAL ANALYSIS OF THE EXTRACT

The polyphenolic mixture present in each extract was examined by two dimensional chromatography using 6% acetic acid and secondary butanol: acetic acid: water (14:1:5)<sup>8</sup> as solvents for the first and the second dimensions respectively. The chromatograms were developed with diazotised-*p*-nitroaniline. The extracts at all different temperatures were analysed for their tans, nontans, (hide powder method) total salts,<sup>10</sup> gum content,<sup>11</sup> sugar<sup>12</sup> and gelatine number.<sup>13</sup>

#### C. TANNING EXPERIMENT

The butt portion of a piece of delimited goat skin was cut into a number of small pieces (3" × 2") and these were then tanned with liquor extracted at different temperatures (both consecutive and separate) within three days, by shaking. The delimited pelt and tannin ratio was kept 2:1 and the ratio of the pelt and tan liquor was kept 1:100 in all the cases. After the completion of tanning, the pieces were dried, cut into small pieces and washed with distilled water for 24 hours with occasional stirring to remove the loosely bound tannin and then dried again in air. The fixed tan of the dried pieces were then determined in the usual way (Table 1).

#### Discussion & results

The present investigation supports the work of Nemec<sup>5</sup> and Roux<sup>7</sup> on pine bark and wattle respectively in that the differential aqueous extractions yield different tan/nontan ratio and different amounts of nontannins. As also observed by Roux,<sup>7</sup> the cold and cool extracts were found clearer and lighter than hot extracted liquor.

From Table 1, it is evident that leaching at 8°C yields an extract of very low tan/nontan ratio. At that temperature almost the same amount of gum as was obtained with other higher temperatures and largest amount of total salts were extracted and these were presumably mainly responsible for high nontans as compared to the tannins extracted. The cold extract also showed lowest gelatine number. On dry bark basis, the yield of extract at 8°C was found to be the lowest and total salt and gum contents were lower than those at other high temperatures (both separate and consecutive). The subsequent 30°C (separate) leach removed almost the same quantity of gum as the previous extraction, much low salt content and increased *T/NT* ratio. The tannins from the extraction showed slightly higher gelatine number than those extracted at previous extraction. The consecutive leach at 30°C removed slightly less amount of gum than the previous extraction, almost half of salt content and very much increased tan-nontan ratio. On the dry

Table 1

ANALYSIS OF THE GORAN LIQUORS EXTRACTED AT VARIOUS TEMPERATURES

Yield (extractable material)	Procter's extraction	8°C	Room temp. (30°C)		80°C	
			(separate)	(consecutive)	(separate)	(consecutive)
						80°C
						(consecutive)
Tans	g./100 g. of dry bark	20.4	1.32	1.68	2.21	1.72
	{ g./100 g. of T.S.	79.7	48.5	53.5	59.3	64.5
	{ g./100 g. of dry bark	16.2	0.61	0.86	1.29	1.06
Nontans	{ g./100 g. of T.S.	20.3	51.4	46.5	40.7	35.5
	{ g./100 g. of dry bark	4.1	0.64	0.74	0.88	0.59
T/NT ratio		3.9	0.94	1.15	1.46	1.8
Total salts	{ m.eq./100 g. of T.S.	134	462.7	443.6	348.5	260.2
	{ m.eq./100 g. of dry bark	27.2	5.77	7.55	7.56	4.28
Gum content	{ g./100 g. of T.S.	17.2	12.1	12.3	12.8	11.4
	{ g./100 g. of dry bark	3.8	0.15	0.19	0.28	0.15
Gelatine number		248.6	279	374	325	401
Degree of tannage of the leathers tanned with various liquors						
		48.5	47.06	49.25	44.93	50.37
						47.06

**Table 2**  
ANALYSIS OF THE COUNTER-CURRENT EXTRACTS  
(per 100 g. of extract)  
(on moisture free basis)

	Counter-current (Room temp.)	Counter-current (hot)
Tannins		
Nontannins	55.8	62.4
T/NT ratio	38.3	33.2
Insolubles	1.45	1.88
Total salts (m. eq./100 g. of extract)	5.8	4.4
Gum content	415	295
Sugar	12.2	13.6
Leaching efficiency $\left( \frac{\text{amount of tannins leached}}{\text{amount of tannins present}} \times 100 \right)$	trace	trace
	92.3	98.5

bark basis, at 30°C the yield of the extract, T/NT ratio, gum content and total salts were more than those obtained at 8°C. The yield of the extract and T/NT ratio at 30°C (consecutive) were found to be more and total salt and gum content to be less than those extracted at 30°C (separate). The hot leach (separate) yielded almost the same gum content, high T/NT ratio and very high gelatine number. The consecutive hot leach at 80°C was very low in gum content and total salt, and had very high gelatine number and T/NT ratio. On dry bark basis, the yield of the extract and tan content at 80°C (both separate and consecutive) were found to be maximum. The consecutive hot leach showed a higher T/NT ratio and less of total salt and gum content.

From Table 1, it is quite evident that even at 80°C (both separate and consecutive) the yield of the extract is very

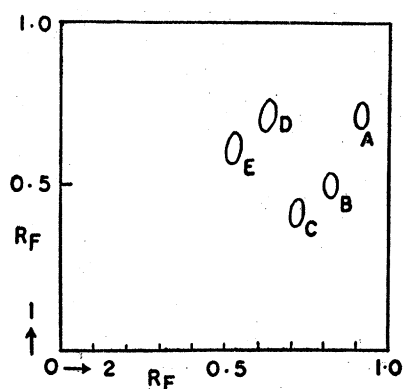
poor as compared to the total yield obtained and consequently tannins, total salt and gums extracted were also very low. From this work it follows that to get a good yield, mangrove bark needs to be leached a number of times by the counter-current technique.

It was observed that in consecutive experiment at 30°C, the yield and tan content were more than at 8°C. Similarly at 80°C, the yield and the tannin content were more than at 30°C. Presumably, the tannins of mangrove, which are mainly in the polymerised form, are slowly soluble in water and most of the tannins could be removed with a number of leachings with water at room temperature. This has been shown in the counter-current experiment. The more the bark would be in contact with water, the more would be the yield and the yield of any leaching would be more than in the previous leaching. In both separate

and consecutive experiments, liquors extracted at 80°C showed highest gelatine number suggesting that higher the temperature of extraction, higher is the particle size of the tannins.

Gum from the dry goran bark was found to be soluble in cold water (8°C) almost to the same extent as at 30°C and 80°C but as sugar is present only in traces, no comparison could be made from the liquors extracted at different temperatures. Maximum salt is extracted during cold leaching (8°C) on total soluble basis; presumably goran contains more of salt of strong acids mainly sodium chloride, and the latter being highly soluble in water, the maximum amount of sodium chloride is extracted during cold leaching as compared to tannins, which are not highly soluble in water.

At 80°C and 30°C (both separate and consecutive) all the mobile constituents A, B, C, D and E (see figure) were visible. But at 80°C in both separate and consecutive experiments only A, B and C were visible and D and E were



1. 6% acetic acid.
2. Sec. butanol: acetic acid: water (14:1:5)

found missing. At higher temperature some of the chromatographically mobile constituents having lower molecular weight presumably get polymerised and become immobile and this might be the reason for the absence of some of the constituents of the liquors after extraction at 80°C. The trailing was found to be more as the temperature is increased.

In the counter-current extract (Table 2) there is not much of difference in  $T/NT$  ratio and gum content, the extract obtained at higher temperature giving slightly higher  $T/NT$  ratio and more of gum. But the total salt of the extract extracted by ordinary counter-current extraction (room temperature) was found to be much more than that of the hot extract. The counter-current extract at room temperature after 6th extraction yielded about 50°Bk strength liquor and the dry extract when analysed was found to contain about 6% less of tannin as compared to the dry extract from liquors extracted at higher temperature. The leaching efficiency (no. of g. of tannin leached per 100 g. tannin) of the cold counter-current extract was found to be slightly less than that of hot extraction suggesting that by counter-current extraction at room temperature it is possible to extract almost all the tannins from the mangrove barks. Higher temperature only involves oxidation in the tannin molecule which makes the leather dark and hard. To extract all the tannins from the mangrove by counter-current technique, first four leachings could be made with ordinary water and the last two leachings with hot water (60°C).

It is observed that by tanning with cold or room temperature leached liquor

(both consecutive and separate) there is slightly higher fixation of tannins by the pelt as compared to the liquors extracted at higher temperature (80°C) proving that in mangrove the liquor extracted at room temperature is always better than the one extracted at higher temperature.

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